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The Estimation of Hamaker Constants of Alcohols and Interfacial Tensions at Alcohol-Mercury Interfaces

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Macroscopic approach of van der Waals attraction theory is employed to calculate the Hamaker constants (A) of two identical short chain aliphatic alcohols in vacuum. Values so obtained are in good agreement with those obtained from the microscopic theory, revealing that the intervening effect is negligibly small in these alcohols. The zero frequency contribution to Hamaker constant *i.e.* $A_{n=0}$ is found to be 5–10% of total Hamaker constant. The dispersion contribution to the surface energy of alcohols has been estimated. Further, the interfacial tensions between alcohol and mercury ($\gamma_{A/M}$) are also calculated. These values compare well with experimentally determined values of $\gamma_{A/M}$, when a correction term for the dipole-induced dipole interaction between alcohol and mercury was introduced in Fowkes' equation for the interfacial tension.

KEY WORDS: Hamaker constant / van der Waals force / Macroscopic method / Surface energy / Interfacial tension / Alcohol / Mercury /

INTRODUCTION

The van der Waals (v.d.w.) forces are quantum mechanical in origin and emanate from the fluctuating electromagnetic field around the atomic dipoles. If a molecule possesses a permanent dipole moment (polar molecule), the interaction between the dipoles lead to the existence of orientation forces. These forces are also called as Keesom forces. A polar molecule may also polarize a nearby neutral molecule and results in an additional induction or Debye force between them. The prerequisite for the existence of these forces is the presence of at least one permanent dipole. However, molecules possessing no permanent dipole moments (non-polar) may also attract each other through the forces called as dispersion forces. Though the time average of the dipole moment in such molecules is zero, yet at any instant there exists a finite fluctuating dipole which polarizes the neighbouring atoms or molecules and results in an attractive force between them. The frequency of fluctuations is in the ultra-violet (u.v.) region and closely related to optical dispersion. Therefore these forces are referred to as dispersion forces. The satisfactory theory to account for these forces was put forward by London^{1,2)} who showed that the v.d.w. interaction energy of two atoms or molecules in free space varies as the inverse sixth power of their separation. Dispersion forces are some times known as the London or London-van der Waals forces. The total v.d.w. force between two atoms or molecules is given by sum of the

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orientation, induction and dispersion forces. The dispersion forces are always present and dominate over the orientation and induction forces except in the case of strongly polar molecules.

The v.d.w. forces are of fundamental importance in the colloid and interface chemistry involving the phenomena such as colloid stability, surface and interfacial tensions, wetting, adhesion and so on. There are two approximate ways of calculating the dispersion force between two condensed bodies, *viz.* microscopic and macroscopic approaches depending on whether the force between the bodies is obtained in terms of their microscopic properties (such as atomic or molecular polarization) or macroscopic properties (such as dielectric permittivity). The original Hamaker's approach starts from the properties of individual molecules (microscopic method) and is based on the assumption that the energy of interaction between two condensed bodies is made-up of the sum of interaction energies between all the atoms. De Boer³⁾ and Hamaker⁴⁾ carried out the summation procedure for geometries of interacting bodies. Hamaker showed that the v.d.w. force is specified by a constant A called as Hamaker constant which depends only on the nature of the materials involved. A great drawback of this method is the assumed additivity of molecular interactions.

Lifshitz and co-workers^{5,6)} enunciated a theory for the interaction between condensed bodies which involves only the bulk material properties *viz.* the optical properties of the interacting materials over the entire electromagnetic spectrum. This is the physically most satisfactory approach for calculating the v.d.w. interactions. As such, the equations derived by Lifshitz are rather difficult to deal with. However, using approximation in the Lifshitz theory, Ninham⁷⁾ and others^{8,9)} have developed a macroscopic theory which is easy to use.

In the present investigation, the macroscopic method of Ninham and Parsegian is used to evaluate the Hamaker constants of alcohols. The Hamaker constants have also been estimated from the microscopic method for making comparison. Furthermore, the Hamaker constants have been used to calculate the interfacial tensions at the alcohol-mercury interfaces.

THE CALCULATING METHODS

Hamaker constants of alcohols

Microscopic procedure:

In microscopic procedure, the magnitude of dispersion force of substance can be expressed in terms of Hamaker constant, which is related to molecular properties by the following equation:

$$A_{11} = \pi^2 N_1^2 C_{11}, \quad [1]$$

where the subscript 11 refers to the interaction in vacuum of two condensed bodies of the same material 1. N_1 is the number of atoms per unit volume and C_{11} is the London dispersion force pair interaction constant. C_{11} can be evaluated from the London equation which makes use of the polarizability and fundamental electron frequency ν_0 :

$$C_{11} = \frac{3}{4} \alpha_{01}^2 h \nu_0, \quad [2]$$

where α_{01} is the static polarizability of atom 1. This equation is based on the single oscillator model of Drude type, so the fluctuation of electron density of atoms in ground state is considered to occur at a single frequency ν_0 characteristic of the substance. London suggested that $h\nu_0$ term in Eq. [2] should be replaced by the ionization potential I . Hence we have

$$C_{11} = \frac{3}{4} \alpha_{01}^2 I, \quad [3]$$

where α_{01} is related to the molar refraction R_0 by the following equation:

$$\alpha_{01} = \frac{3R_0}{4\pi N_a}, \quad [4]$$

where N_a is the Avogadro number. In our calculations R_0 was obtained from the refractive equivalents¹⁰⁾ corresponding to the sodium line for different atoms present in the molecule.

Macroscopic procedure:

The non-retarded v.d.w. free energy \bar{G} between two identical isotropic small particles at a short distance of separation D in a free space is given by McLachlan^{11,12)}:

$$\bar{G} = -\frac{C_{11}}{D^6} = -\frac{6kT}{D^6} \sum'_{n=0,1,\dots} \alpha_1^2(i\omega_n), \quad [5]$$

where

$$C_{11} = 6kT \sum'_{n=0,1,\dots} \alpha_1^2(i\omega_n). \quad [6]$$

Here, $\alpha(i\omega_n)$ represents the polarizability of particle 1 as a function of imaginary frequency $i\omega_n$, where

$$\omega_n = n(2\pi kT/h). \quad [7]$$

The polarizability consists of three terms corresponding to the respective contribution from rotational, vibrational and electronic frequencies *i.e.*

$$\alpha_1(i\omega_n) = \alpha^{bd}(i\omega_n) + \alpha^{vb}(i\omega_n) + \alpha^{ev}(i\omega_n). \quad [8]$$

Fowkes¹³⁾ derived an expression for the v.d.w. interaction free energy between two bodies by summation of pair potential and is given as

$$G = -1.2\pi N_1^2 C / 2D^2. \quad [9]$$

Substituting Eq. [6] into Eq. [9] we get

$$G = -(3.6\pi kT/D^2) \sum'_{n=0,1,\dots} N_1^2 \alpha_1^2(i\omega_n). \quad [10]$$

According to the classical electro-magnetic theory, the volume polarizability $N_1\alpha_1(i\omega_n)$ in vacuum is related to the dielectric permittivity $\epsilon_1(i\omega_n)$ of the material by the following equation^{8,14)}

$$N_1\alpha_1(i\omega_n) = \frac{1}{2\pi} \left[\frac{\varepsilon_1(i\omega_n) - 1}{\varepsilon_1(i\omega_n) + 1} \right]. \quad [11]$$

Substituting Eq. [11] into Eq. [10] we get

$$G = -\frac{3.6kT}{4\pi D^2} \sum_{n=0,1,\dots}^{\infty} \left[\frac{\varepsilon_1(i\omega_n) - 1}{\varepsilon_1(i\omega_n) + 1} \right]^2. \quad [12]$$

It follows from Eq. [12] that

$$G_{n=0} = -\frac{3.6kT}{8\pi D^2} \left[\frac{\varepsilon_1(0) - 1}{\varepsilon_1(0) + 1} \right]^2, \quad [13]$$

where $\varepsilon(0)$ is the static dielectric constant. Comparing Eqs. [1] and [9] we obtain

$$G = -\frac{1.2A}{2\pi D^2}, \quad [14]$$

where

$$G_{n=0} = -\frac{1.2A_{n=0}}{2\pi D^2} \quad [15]$$

and

$$G_{n>0} = -\frac{1.2A_{n>0}}{2\pi D^2}. \quad [16]$$

Combining Eqs. [13] and [15] we get

$$A_{n=0} = \frac{3kT}{4} \left[\frac{\varepsilon_1(0) - 1}{\varepsilon_1(0) + 1} \right]^2. \quad [17]$$

For non-zero frequency term the summation in Eq. [5] necessitates the evaluation of $\alpha_1(i\omega_n)$ at the discrete frequencies given by Eq. [7]. As can be explained by Eq. [22], in general the major magnitude of $N_1\alpha_1(i\omega_n)$ comes from the electronic contribution *i.e.* dispersion contribution. Using $dn = \frac{\hbar}{2\pi kT} d\omega$ and replacing the summation in Eq. [12] by integration we get

$$G_{n>0} = -\frac{3.6\hbar}{8\pi^2 D^2} \int_{\omega_1}^{\infty} \left[\frac{\varepsilon_1(i\omega_n) - 1}{\varepsilon_1(i\omega_n) + 1} \right]^2 d\omega. \quad [18]$$

At zero temperature, ω_1 is also zero so that

$$G_{n>0} = -\frac{3.6\hbar}{8\pi^2 D^2} \int_0^{\infty} \left[\frac{\varepsilon_1(i\omega_n) - 1}{\varepsilon_1(i\omega_n) + 1} \right]^2 d\omega. \quad [19]$$

Eq. [19] is also true even at finite temperature provided the contributions from the frequencies below ω_1 are very small. Comparing Eqs. [16] and [19] we obtain

$$A_{n>0} = \frac{3\hbar}{4\pi} \int_0^{\infty} \left[\frac{\varepsilon_1(i\omega_n) - 1}{\varepsilon_1(i\omega_n) + 1} \right]^2 d\omega. \quad [20]$$

This expression involves the dielectric permittivity as a function of the imaginary frequency in radian/second. In order to use the above expression for making quantitative calculations a convenient representation of the dielectric permittivity is essential. The dielectric permittivity is exactly expressed by the Kramers-Kronig equation, but

as shown by Ninham and Parsegian^{7,15,16} the following equation is used to a good approximation

$$\varepsilon(i\omega_n) = 1 + \sum_r \frac{C_{\text{rot}}}{1 + \left(\frac{\omega_n}{\omega_{\text{rot}}}\right)^2} + \sum_j \frac{C_j}{1 + \left(\frac{\omega_n}{\omega_j}\right)^2}. \quad [21]$$

This equation holds good for frequencies up to the u.v. region. The second term of the right hand side of Eq. [21] is due to the Debye rotational relaxation coming from the rotation of permanent dipoles in the microwave region. The third term denotes the contributions of vibrational and electronic absorption in the i.r. and u.v. regions: this term gives rise to the London dispersion interaction. In Eq. [21] ω_{rot} is a relaxation frequency associated with the rotation of dipoles, and ω_j is associated with electronic and vibrational frequencies. These may be obtained from various spectroscopic data and the constants C_{rot} and C_j are obtained from the experimental dielectric data.

Splitting the i.r. and u.v. contributions in Eq. [21] we have

$$\varepsilon(i\omega_n) = 1 + \sum_r \frac{C_{\text{rot}}}{1 + \left(\frac{\omega_n}{\omega_{\text{rot}}}\right)^2} + \sum_k \frac{C_{ir}}{1 + \left(\frac{\omega_n}{\omega_{ir}}\right)^2} + \sum_m \frac{C_{uv}}{1 + \left(\frac{\omega_n}{\omega_{uv}}\right)^2}. \quad [22]$$

Since $\omega_{uv} \gg \omega_{ir} > \omega_{\text{rot}}$, the major contribution to $\varepsilon(i\omega_n)$ comes from the u.v. region when $n > 0$, so that

$$\varepsilon(i\omega_n) = 1 + \sum_m \frac{C_{uv}}{1 + \left(\frac{\omega_n}{\omega_{uv}}\right)^2}, \quad [23]$$

where C_{uv} in Eq. [23] is approximated to $n^2 - 1$, and n is the refractive index of the material in visible region.¹⁵ Hence we may rewrite Eq. [23] as

$$\varepsilon(i\omega_n) = 1 + \sum_m \frac{n^2 - 1}{1 + \left(\frac{\omega_n}{\omega_{uv}}\right)^2}. \quad [24]$$

For one term dispersion in the u.v. region, Eq. [24] takes the form

$$\varepsilon(i\omega_n) = 1 + \frac{n^2 - 1}{1 + \left(\frac{\omega_n}{\omega_{uv}}\right)^2}. \quad [25]$$

Substituting Eq. [25] into Eq. [20] and integrating using the definite integral

$$\int_0^\infty \frac{dx}{(a^2 + x^2)^2} = \frac{\pi}{4a^3}, \quad [26]$$

we arrive at

$$A_{n>0} = \frac{3\hbar\omega_{uv}(n^2 - 1)^2}{16\sqrt{2}(n^2 + 1)^{3/2}}. \quad [27]$$

Eq. [27] together with Eq. [17] gives the total magnitude of the Hamaker constant. *i.e.* $A = A_{n=0} + A_{n>0}$. Eq. [27] is an approximate expression valid for media, which follows one term dispersion formula with the peak at ω_{uv} in the u.v. region.

For metals, Eq. [21] takes the limiting form between far u.v. and soft X-ray

regions¹⁶⁾ as

$$\varepsilon(i\omega_n) = 1 + \frac{4\pi N e^2}{m_e \omega_n^2} = 1 + \left(\frac{\omega_p}{\omega_n} \right)^2, \quad [28]$$

where e , m_e and N are the charge, effective mass and density of electron and ω_p is the plasma frequency defined by

$$\omega_p^2 = \frac{4\pi N e^2}{m_e}.$$

The relation between the Hamaker constant and interfacial tension:

The dispersion force interaction energy G^d between two identical bodies e.g. non-polar hydrocarbons consists of a temperature dependent (entropic) term $G_{n=0}^d$ and a temperature independent term $G_{n>0}$ and is related to the work of cohesion by

$$G^d = G_{n=0}^d + G_{n>0} = -2\gamma^d, \quad [29]$$

where γ^d is the dispersion component of surface energy. Combining Eqs. [29] and [14] we get

$$\gamma^d = \frac{1.2 A^d}{4\pi D^2}, \quad [30]$$

where A^d is the dispersion force contribution to the total Hamaker constant. It follows from Eq. [30] that it is possible to calculate γ^d by knowing the values of A^d and D . Further, Fowkes¹⁷⁾ proposed an expression for the interfacial tension γ_{12} between two immiscible non-polar liquids 1, 2 in terms of the surface tension (energy) and γ^d :

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d}, \quad [31]$$

where γ_1 and γ_2 are the surface tensions of two individual liquids and γ_1^d and γ_2^d are the dispersion force contribution to the surface energy of liquids 1 and 2, respectively. If we use this equation for the calculation of interfacial tension between alcohol and mercury, higher values are obtained. This is explained by the fact that in deriving Eq. [31] it was assumed that the intermolecular attraction at the alcohol-mercury interface is only due to the London dispersion force. If one of the bodies was polar and had a permanent dipole as in the case of alcohol-mercury interface, Eq. [31] is always not true because other forces act at the interface in addition to the dispersion force. In such system we should account for the permanent dipole contribution of alcohol. Hence Eq. [31] for alcohol-mercury system is modified as

$$\gamma_{A/M} = \gamma_A + \gamma_M - 2\sqrt{\gamma_A^d \gamma_M^d} - 2\sqrt{\gamma_A^{pd} \gamma_M^{pd}}, \quad [32]$$

where the subscripts A and M refer to alcohol and mercury, respectively, and γ_A^{pd} is the permanent dipole contribution to the surface energy of alcohol which is given by

$$\gamma_A^{pd} = \frac{1.2 A^{pd}}{4\pi D^2}. \quad [33]$$

Here

$$A^{pd} = A_{n=0}^{pd} + A_{n>0}^{pd}. \quad [34]$$

Thus knowing the surface tensions, γ^a and γ_A^{pa} we can predict the value of interfacial tension between alcohol and mercury. Now the problem is to calculate γ_A^{pa} . This is accomplished as follows.

In case of one frequency absorption each for ω_{rot} , ω_{ir} and ω_{uv} Eq. [22] takes the form

$$\varepsilon(i\omega_n) = 1 + \frac{C_{rot}}{1 + \left(\frac{\omega_n}{\omega_{rot}}\right)^2} + \frac{C_{ir}}{1 + \left(\frac{\omega_n}{\omega_{ir}}\right)^2} + \frac{C_{uv}}{1 + \left(\frac{\omega_n}{\omega_{uv}}\right)^2}. \quad [35]$$

Let the second, third and fourth terms of Eq. [35] be denoted as $\varepsilon_{rot}(i\omega_n)$, $\varepsilon_{ir}(i\omega_n)$ and $\varepsilon_{uv}(i\omega_n)$, respectively, so that Eq. [35] can be rewritten as

$$\varepsilon(i\omega_n) = 1 + \varepsilon_{rot}(i\omega_n) + \varepsilon_{ir}(i\omega_n) + \varepsilon_{uv}(i\omega_n). \quad [36]$$

Substituting Eq. [36] into Eq. [11] we have

$$\begin{aligned} N_1 \alpha_1(i\omega_n) &= \frac{1}{2\pi} \left[\frac{\varepsilon_{rot}(i\omega_n) + \varepsilon_{ir}(i\omega_n) + \varepsilon_{uv}(i\omega_n)}{2 + \varepsilon_{rot}(i\omega_n) + \varepsilon_{ir}(i\omega_n) + \varepsilon_{uv}(i\omega_n)} \right] \\ &= N_1 \alpha_1^{pd}(i\omega_n) + N_1 \alpha_1^{ir}(i\omega_n) + N_1 \alpha_1^{uv}(i\omega_n). \end{aligned} \quad [37]$$

The rotational frequency contribution (permanent dipole) only, to the volume polarizability *i.e.* $N_1 \alpha_1^{pd}(i\omega_n)$ is given by

$$N_1 \alpha_1^{pd}(i\omega_n) = \frac{1}{2\pi} \left[\frac{\varepsilon_{rot}(i\omega_n)}{2 + \varepsilon_{rot}(i\omega_n) + \varepsilon_{ir}(i\omega_n) + \varepsilon_{uv}(i\omega_n)} \right]. \quad [38]$$

Substituting Eq. [38] into Eq. [10] we obtain the permanent dipole contribution to the interaction free energy

$$G^{pd} = -\frac{3.6kT}{4\pi D^2} \sum_{n=0,1,\dots}^{\infty} \left[\frac{\varepsilon_{rot}(i\omega_n)}{1 + \varepsilon(i\omega_n)} \right]^2. \quad [39]$$

Hence G^{pd} at $n=0$ is given by

$$G_{n=0}^{pd} = -\frac{3.6kT}{8\pi D^2} \left[\frac{\varepsilon_{rot}(0)}{1 + \varepsilon(0)} \right]^2. \quad [40]$$

Combining Eqs. [40] and [15] we get

$$A_{n=0}^{pd} = \frac{3}{4} kT \left[\frac{\varepsilon_{rot}(0)}{1 + \varepsilon(0)} \right]^2. \quad [41]$$

Replacing the summation in Eq. [39] by integration and using zero temperature approximation we obtain

$$G_{n>0}^{pd} = -\frac{3.6\hbar}{8\pi^2 D^2} \int_0^\infty \left[\frac{\varepsilon_{rot}(i\omega_n)}{1 + \varepsilon(i\omega_n)} \right]^2 d\omega. \quad [42]$$

Comparison of Eqs. [42] and [16] leads to

$$A_{n>0}^{pd} = \frac{3\hbar}{4\pi} \int_0^\infty \left[\frac{\varepsilon_{rot}(i\omega_n)}{1 + \varepsilon(i\omega_n)} \right]^2 d\omega. \quad [43]$$

Since $\varepsilon(i\omega_n) \gg \varepsilon_{rot}(i\omega_n)$, $A_{n=0}^{pd} \gg A_{n>0}^{pd}$ so that $\gamma_{n=0}^{pa} \gg \gamma_{n>0}^{pa}$. Hence from Eq. [34] it follows that $A_{n=0}^{pa}$ may be taken as A^{pa} . With the knowledge of A^{pa} and D it is thus possible to estimate the value of γ_A^{pa} (Eq. [33]) which is required in evaluating the interfacial tension.

EXPERIMENTAL

Surface tensions of alcohols were obtained from the Handbook of Chemistry and Physics.¹⁰⁾ Interfacial tension between alcohol and mercury was determined by the drop volume method. Alcohols *viz.* methanol, ethanol, *n*-propanol, *n*-butanol, isobutanol, sec-butanol and *n*-pentanol used for the measurement of interfacial tensions were of guaranteed reagent grade. The weight of fixed number of drops of mercury which were slowly detached from the tip of a vertical capillary tube into alcohol is determined, from which the average weight and hence the volume per drop was calculated. The interfacial tension $\gamma_{A/M}$ was calculated by using the Harkins-Brown formula^{18,19)}:

$$\gamma_{A/M} = \frac{V(d_M - d_A)gF}{2\pi r}, \quad [44]$$

where V is the drop volume, d_M and d_A are densities of mercury and alcohol respectively, r the radius of capillary tip, and g the acceleration due to gravity. F is the Harkins-Brown correction factor and is a function of $r/V^{1/3}$. Taking ethyl alcohol as a reference alcohol and using the literature value of $\gamma_{A/M}$ between ethyl alcohol and mercury,¹⁷⁾ the parameter F/r was decided. The same value of F/r ($=750$) was used for the calculations of $\gamma_{A/M}$ between other alcohols and mercury. The tip of the capillary was made hydrophobic by treating with 10% solution of dimethyldichlorosilane in toluene for ensuring wetting of capillary tip by alcohols. The sensitivity of balance use for measuring the weight of mercury drops was ± 1 mg. Thus the accuracy in measurement of interfacial tension was about ± 8 dyne/cm. The experiments were carried out at $20 \pm 0.3^\circ\text{C}$.

CALCULATIONS, RESULTS AND DISCUSSION

Hamaker constant:

In macroscopic approach the Hamaker constant between two identical alcohols in vacuum was calculated by Eqs. [17] and [27]. The values of $\epsilon(0)$ and ω_{uv} were obtained from the literature.^{11,20)} Alcohols exhibit the first characteristic absorption peak around $\omega_{uv} = 1.6 \times 10^{16}$ rad/sec. For methanol and ethanol the first peak is predominant. But for other alcohols contribution from the successive peak become important. A peak corresponding to the maximum absorption was generally used in our calculation. When there were two predominant peaks, the root mean square was taken for obtaining one term ω_{uv} value.

The Hamaker constants so obtained are summarized in Table I together with other parameters used in the calculations. The Hamaker constants calculated using Eq. [1] (microscopic approach) is also shown in Table I, and were in reasonable agreement with those obtained from the macroscopic method, indicating that the intervening effect is negligible in case of these alcohols. The term $A_{n=0}$ in the Hamaker constant of macroscopic method is basically entropic, for it includes the thermal energy kT . Employing the macroscopic method, Ninham and Parsegian^{16,20)} estimated the

The Estimation of Hamaker Constants and Interfacial Tensions

Table I. Hamaker Constants and Related Data at 20°C

Compounds	MeOH	EtOH	n-PrOH	n-BuOH	iso-BuOH	sec-BuOH	n-PentOH	Water
Parameters								
$\epsilon(0)$	33.6	25.7	21.8	17.8	18.7	15.5	15.8	80.0
$C_{uv}=n^2-1$	0.7657	0.8526	0.9182	0.9581	0.9430	0.9471	0.9884	0.78*
$\omega_{uv} (\times 10^{16} \text{ rad/s})$	1.6667	1.8080	1.7350	1.8125	1.9994	1.9371	1.8566	1.906*
Macroscopic $A_{n>0}$	2.97	3.81	4.10	4.57	4.92	4.80	4.91	4.48
($\times 10^{-13} \text{ erg}$) $A_{n=0}$	0.27	0.26	0.25	0.24	0.24	0.23	0.24	0.29
A	3.24	4.07	4.35	4.81	5.16	5.03	5.15	4.77
Microscopic A								3.28-
($\times 10^{-13} \text{ erg}$)	3.06	3.91	4.24	4.73	5.31	5.04	5.15	6.40

* $C_{ir}=3.4$

$\omega_{ir}=5.666 \times 10^{14} \text{ rad/s}$.

Hamaker constants of hydrocarbon-water system and indicated that $A_{n=0}$ terms for those materials consist of 90% entropic contribution. Assuming the same entropy contribution in $A_{n=0}$ term for alcohol it is found that about 5–10% of the total Hamaker constant is due to the entropic contribution. However, the major share to the constant comes from the non-zero frequency term which is enthalpic and of dispersion contribution.

Interfacial tension:

The knowledge of the Hamaker constant provides the possibility of applying it to predict the interfacial tension (energy) of the alcohol-mercury interface. The interfacial tension was calculated using Eq. [32]. The surface energies γ_A and γ_M are taken from the reference¹⁰⁾ as there is no defined way to estimate theoretically the respective contribution to the surface energy from chemical and metallic bonds except the v.d.w. contribution. The v.d.w. surface energy of metals may be calculated from Eq. [30] which makes use of A^d and D . The Hamaker constant of mercury may be calculated by employing Eqs. [12], [14] and [28]. But the application of Eq. [28] is imperfect because of the necessity to consider contributions from interband transitions and collective oscillations.²²⁾ Hence the experimental value of γ_M^d (200 erg/cm²) obtained from the contact angle measurement¹⁷⁾ is used in the present estimation of interfacial tension.

The $\epsilon(0)$ value of alcohols decreases with increase in frequency and beyond the relaxation frequency it reaches a very small value in the m.w. region. The difference between these two values of dielectric constants gives the measure of C_{rot} . These values, for different alcohols were obtained from the literature.²³⁾ It follows from Eqs. [35] and [36] that at zero frequency $\epsilon_{rot}(0)=C_{rot}$.

We need the value of separation D for calculating $\gamma_A^{p^d}$ and γ_A^d . This value is model dependent. In the present calculations molecules were treated as sphere of diameter D , packed closely in a rhomboidal dodecahedron so that the volume occupied

by the sphere is $\pi/3\sqrt{2}$ of the total volume.²⁴⁾

Hence

$$\frac{\pi}{6}D^3 = \frac{\pi}{3\sqrt{2}} \cdot \frac{M}{N_a d_A},$$

where M is the molecular weight, N_a the Avogadro number and d_A the density. The diameter D obtained from the above equation was equated to the centre to centre separation. The values of $\gamma_{n=0}^{pd}$ are calculated by using Eqs. [33] and [41]. The knowledge of $A_{n=0}^{pd}$ also gives the contribution of the dispersion force in $A_{n=0}$ term, i.e. $A_{n=0}^d$ of alcohols:

$$A_{n=0}^d = A_{n=0} - A_{n=0}^{pd}.$$

Thus the total dispersion Hamaker constant for alcohols is written as

$$A^d = A_{n=0}^d + A_{n>0}^d.$$

The evaluation of γ_A^d is accomplished from A^d and D . The value of γ_A^{pd} and γ_A^d thus determined are shown in Table II, and it is found that the dominant contribution to the surface energy of alcohols comes from γ_A^d . The knowledge of these two contributions also leads to the possibility of calculating the Debye contribution to the surface energy of alcohols from the root mean square values of γ_A^d and γ_A^{pd} .

Table II. Calculated and Experimental Values of Interfacial Tensions and Related Parameters at 20°C

Compounds	MeOH	EtOH	n-PrOH	n-BuOH	iso-BuOH	sec-BuOH	n-PentOH
Parameters							
D (Å)	4.56	5.15	5.60	5.99	5.97	5.99	6.33
C_{rot} *	28.2	20.6	17.3	14.7	15.5	12.0	11.9
ω_{rot} ($\times 10^9$ rad/s) *	17.125	6.9767	1.8867	1.7605	1.2642	2.0255	1.3953
$A_{n=0}^{pd}$ ($\times 10^{-13}$ erg)	0.20	0.18	0.18	0.19	0.19	0.16	0.15
γ_A^{pd} (erg/cm ²)	0.92	0.65	0.53	0.49	0.50	0.43	0.36
$A_{n=0}^d$ ($\times 10^{-13}$ erg)	0.07	0.08	0.07	0.05	0.05	0.07	0.09
A^d ($\times 10^{-13}$ erg)	3.04	3.89	4.17	4.62	4.97	4.87	5.00
γ_A^d (erg/cm ²)	13.96	14.01	12.70	12.30	13.32	12.96	11.92
γ_A (erg/cm ²) #	22.6	22.7	23.8	24.6	23.0	23.0	25.7
$\gamma_{A/M}^{calc}$ (dyne/cm)	374	378	386	390	384	387	395
$\gamma_{A/M}^{exptl}$ (dyne/cm)	367 \pm 8	387 \pm 8	392 \pm 8	390 \pm 8	400 \pm 8	376 \pm 8	395 \pm 8

* P. C. Brot, M. Magat, and L. Reinisch, *Kolloid-Z.*, **134**, 101 (1953).

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$\gamma_M = 484$ erg/cm²; $\gamma_M^d = 200$ erg/cm²

Substituting the values of γ_A , γ_M , γ_A^d , γ_M^d , and γ_A^{pd} in Eq. [32] we arrive at the semi-theoretical values of interfacial tension between the alcohol-mercury interface. The interfacial tension with the related parameters used here has been also tabulated in Table II along with the experimentally obtained interfacial tensions. It can be seen in Table II that the calculated interfacial tensions agree closely with the experimental values within the experimental error, indicating that the estimated Hamaker

constants are reasonable. This agreement also leads to the conclusion that the interaction at the alcohol-mercury interface consists mainly of the dispersion and Debye forces, and that the interaction due to other forces is negligible.

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